Evidence for strong Coulomb interactions in alkali-TCNQ (tetracyanoquinodimethan) salts*

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Measurements are reported of the dielectric function at optical and microwave frequencies in pure single crystals of potassium tetracyanoquinodimethan [$K^+(TCNQ)^-$], as well as measurements of the microwave conductivity and electron spin resonance. The results indicate that $K^+(TCNQ)^-$ is in the intermediate- to strong-coupling regime with electron-electron Coulomb repulsion and electron-energy bandwidth of the same magnitude. The spin-resonance studies show a single narrow line with no evidence of extra dipolar-split sidebands.

INTRODUCTION

An important aspect of the analysis of the properties of the TCNQ (tetracyanoquinodimethan) based ionic charge-transfer salts involves the strength of the electron-electron Coulomb repulsion, U_{eff}, relative to the electronic energy bandwidth W.[1] Under certain circumstances, the Coulomb interaction in a solid may be approximated by a short-range effective interaction U_{eff}. The relative short range arises in the conventional theory of metals from plasmon screening of the long-range forces. Such screening will persist in the presence of a small single-particle energy gap, E_{sp}, so long as $E_{sp} \ll \hbar\omega_p$, where ω_p is the electron plasma frequency. In such cases, so long as the measuring frequency ω (e.g., in an optical absorption or reflection experiment) is such that $\omega \ll \omega_p$, a localized effective interaction can be an excellent approximation, and U_{eff} can be further reduced by nearby polarization contributions. However, if $U_{eff} \sim \hbar\omega_p$, the concept of a localized effective interaction has little meaning and the full long-range interaction must be considered.

In the limit of weak interactions, the electronic system can be treated in terms of single-particle band theory. This treatment leads to metallic or simple semiconducting behavior depending on whether the chain structure is uniform or distorted so as to cause an energy gap at the Fermi wave number. In the opposite, strong-coupling limit, the electronic wave functions are localized by the electron-electron repulsion, the Coulomb interaction is not effectively screened by plasmons, and a relatively large energy gap (of order $U_{eff} \lesssim \hbar\omega_p$ in the limit $U \gg W$) appears in the single-particle excitation spectrum. However, in this localized strong-coupling regime, the electron-spin degrees of freedom remain, so that collective spin excitations, i.e., triplet excitons or spin waves, appear at low energies. For a uniform chain system, the spin-wave spectrum has $\epsilon_q \to 0$ as $q \to 0$ whereas, in the strongly dimerized structure, the spectrum is like that of triplet excitons with an energy gap at $q = 0$. The weak- and strong-coupling limiting cases are shown schematically in Figs. 1(a) and 1(b), respectively. Figure 1(a) shows the single-particle excitation spectrum of a simple dimerized semiconductor ($U_{eff} = 0$), and Fig. 1(b) shows the collective spin-wave modes in the gap for the general case of a strong-coupling, nonuniform chain.[2] This qualitative picture must be kept in mind whenever an attempt is made to characterize a given system in terms of strong or weak Coulomb interaction. The general signature of relatively strong interactions ($U_{eff}/W \gtrsim 1$) is the difference between the single-particle energy gap E_{sp} and the collective mode gap E_m in Fig. 1(b).

The apparent simplicity of the alkali-TCNQ salts has led many workers[3] to attempt to establish this family as a prototype system. Low-temperature heat-capacity measurements[4] do indicate a class of simple ionic salts in which the Debye temperatures follow the simple relation $\Theta_D \propto (M_A + M_{TCNQ})^{-1/2}$, where M_A is the mass of the alkali and M_{TCNQ} that of the TCNQ molecule. Nuclear quadrupole resonance[5] studies clearly establish the ionic state with essentially complete electron transfer. The electrical conductivity shows semiconducting behavior ($\sigma = \sigma_0 e^{-\Delta/kT}$) where $\Delta \sim 0.35$ eV.[6]

Kommandeur and co-workers[3] have carried out extensive measurements of the temperature dependence of the magnetic susceptibility through spin-resonance studies in these alkali salts. They analyze their results in terms of simple semiconductor theory [Fig. 1(a)] assuming that the magnetism originates from the single-particle excitations across the gap. Changes in the activation energy were attributed to structural changes driven by the electron-lattice interaction. The central result of their analysis was a determination of the magnetic activation energy Δ_M. In every case, they find $\Delta_M < \Delta_{sp}$ where Δ_{sp} is obtained from the
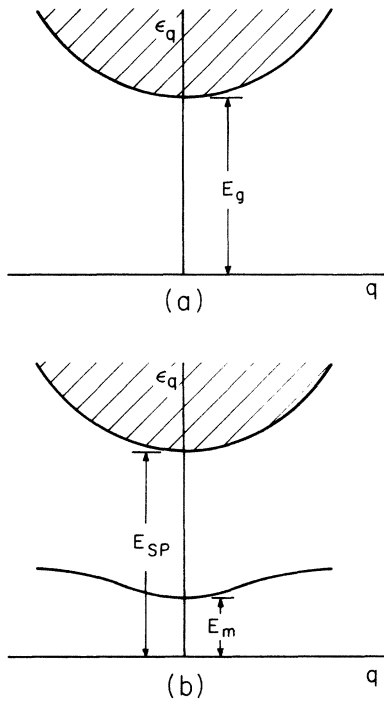
FIG. 1. Schematic single-particle excitation spectra of (a) weak-coupling simple dimerized semiconductor $(U_{eff}=0)$; (b) strong-coupling nonuniform chain, showing collective spin-wave modes in the single-particle gap.

conductivity. This inequality was used to infer that these systems more properly fall into the intermediate- to strong-coupling regime[7] [Fig. 1(b)] rather than being simple semiconductors as stated by Kommandeur et al.[3] However, it can be argued that the activation energy as obtained from the conductivity is not a true indication of Δ_{sp} since the mobility of the excited carriers could be activated either because of disorder due to impurities, etc., or polaron effects. Consequently, an independent measurement of $\Delta_{sp} = \frac{1}{2} E_{sp}$ (and its temperature dependence) is required.

The dielectric function $\epsilon(\omega)$ provides a direct measure of Δ_{sp} which is not sensitive to the various mechanisms which might lead to activated mobilities. We write[8]

$$\epsilon(\omega) = \epsilon_{core} + \omega_p^2/(\omega_{sp}^2 - \omega^2 - i\omega/\tau) , \qquad (1)$$

where ϵ_{core} is the residual dielectric constant at high frequency arising from core polarizability, τ is the electronic relaxation time (assumed independent of frequency), ω_{sp} is the single-particle gap frequency, and ω_p is the plasma frequency with $\omega_p^2 = 4\pi N e^2/m^*$, where N is the electron density and m^* is the effective mass. In the limit $\omega \to 0$, this reduces to

$$\epsilon(0) = \epsilon_{core} + \hbar^2 \omega_p^2/E_{sp}^2 , \qquad (2)$$

where $E_{sp} = \hbar\omega_g$ is the minimum direct single-particle gap.[9] Equations (1) and (2), although approximate, can be applied with reasonable accuracy to real systems by identifying ω_{sp} as an average direct gap and using an effective mass in ω_p.[8] In one-dimensional materials such as the alkali-TCNQ salts, the high density of states at the band edges is expected to dominate the oscillator-strength matrix elements, and Eq. (1) should be a good approximation with ω_g the minimum direct band gap (within a constant of order unity).[9] The plasma frequency and thus the dielectric constant are in general anisotropic, reflecting the anisotropy in the intermolecular transfer integral. For measurement of E_{sp}, ϵ should be measured along the conducting axis (the 1-d chain axis of the crystal). Equation (2) has been verified through detailed studies of the temperature dependence of the anisotropic dielectric constant in tetrathioful-valinium tetracyanoquinodimethan [(TTF) (TCNQ)].[9]

We report in this communication measurements of the dielectric function at optical and microwave frequencies in pure single crystals of $K^+(TCNQ)^-$. The magnitude and temperature dependence of the microwave dielectric constant indicate a single-particle energy gap consistent with the value obtained from the conductivity, thus placing $K^+(TCNQ)^-$ in the intermediate coupling regime [Fig. 1(b)] with $E_{sp} > E_m$. Analysis of the polarized reflectance spectra in the visible and near infrared leads to the same result. The relative values of the gap frequency and the plasma frequency as measured optically confirm the intermediate- to strong-coupling description of this material. In addition, spin-resonance studies on this pure material show a single narrow line $(g = 2)$ with no evidence of sideband resonances as observed by Kommandeur and co-workers[3,10] and attributed to intrinsic exciton states.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Tetracyanoquinodimethan (TCNQ) was prepared under careful experimental conditions as described previously.[11] Single crystals of $K^+(TCNQ)^-$ were grown from solution in multiply distilled CH_3CN using a U-tube diffusion technique by placing ultra-pure anhydrous KI (Alfa Inorganics) in one arm of the diffusion tube and TCNQ in the other arm.

Analysis. Calculated: C, 59.24; H, 1.66; N, 23.03; K, 16.07; found: C, 59.27; H, 1.68; N, 23.03; K, 15.92.

The dielectric constant (ϵ_1) and the room-temperature microwave conductivity were measured using the cavity perturbation technique of Buravov and Shchegolev[12] in which the frequency shift and change in half-width are measured to determine

both the real and imaginary parts of the dielectric function $\epsilon_1 + i\epsilon_2$. The needle-shaped sample (dimensions $3.34 \times 0.21 \times 0.13$ mm) was placed in a rectangular cavity operating in the TE_{101} mode with resonant frequency of 10.4 GHz. As an independent check on the technique, the dielectric constant of single-crystal N-methylphenazinium-tetracyanoquinodimethan [(NMP)(TCNQ)] was measured and found to be $\epsilon_1(7K) = 350 \pm 50$ in excellent agreement with results reported by Shchegolev et $al.$[12] The spin-resonance measurements were carried out at x band using a standard Varian ESR spectrometer.

Polarized reflectance spectra were measured in the visible and near infrared using a Beckman DK-2 spectrophotometer with a specially constructed specular reflectance attachment as described earlier.[13] Large single crystals of $K^+(TCNQ)^-$ with well-developed faces larger than the beam size of 1.5×3 mm were mounted on a translatable and tiltable sample holder to facilitate precise alignment in the spectrophotometer beam. The instrument baseline was calibrated using evaporated gold and silver mirrors.

RESULTS AND DISCUSSION

The room-temperature reflectance spectra for light polarized parallel and perpendicular to the chain axis are shown in Fig. 2. The polarization and frequency of these peaks are in agreement with polarized absorption spectra reported by Hiroma et $al.$[14] The peaks in the transversely polarized spectrum were assigned by Hiroma et $al.$[14] to local excitation modes of the $TCNQ^-$ ions. Hiroma et $al.$ also identified a charge-transfer band at about 1 eV corresponding to motion of electrons along the TCNQ chain. Such an analysis is consis-
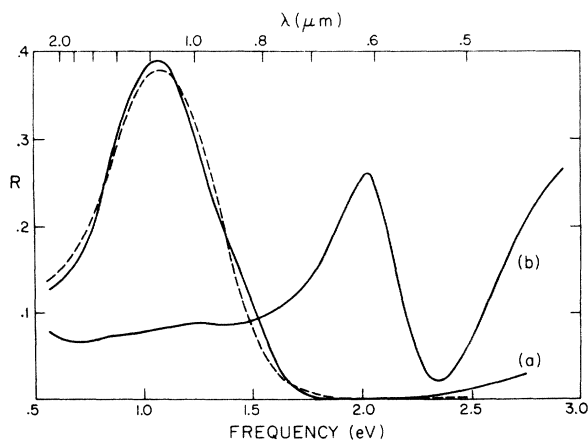
tent with the results presented here.

The most striking features of the parallel-polarized spectrum are the plasmalike edge at 0.7 μm and the steady decrease in reflectance at long wavelengths suggestive of a semiconducting energy gap. These features are incorporated in a dielectric function of the form of Eq. (1). In terms of the real and imaginary parts of ϵ, the reflectance is given by

$$R = \frac{1 + |\epsilon| - [2(|\epsilon| + \epsilon_1)]^{1/2}}{1 + |\epsilon| + [2(|\epsilon| + \epsilon_1)]^{1/2}}, \qquad (3)$$

where $|\epsilon| = (\epsilon_1^2 + \epsilon_2^2)^{1/2}$. The parameters ϵ_{core}, ω_p, ω_{sp}, and τ were determined by a least-squares computer fit of Eqs. (1) and (3) to the experimental data in the region from 0.5 to 2.2 μm. The best fit, shown as the dashed line in Fig. 1, was observed with $\epsilon_{core} = 1.47$, $\omega_p = 2.5 \times 10^{15}$ sec^{-1} ($\hbar\omega_p = 1.65$ eV), $\omega_{sp} = 1.4 \times 10^{15}$ sec^{-1} ($E_{sp} = 0.9$ eV), and $\tau = 2.3 \times 10^{-15}$ sec. The fit is seen to be good, and inclusion of a weak frequency dependence of the scattering time would improve the fit somewhat.

The microwave dielectric constant measured over the temperature range $4.2 < T < 350$ K was independent of temperature with a value of $\epsilon_1 = 6 \pm 1$ as shown in Fig. 3. The room-temperature value is in good agreement with that obtained by Vlasova et $al.$[15] on powder samples.

The room-temperature microwave conductivity of 3×10^{-4} $(\Omega\,cm)^{-1}$ is in close agreement with the dc value of 1×10^{-4} $(\Omega\,cm)^{-1}$ obtained by Kepler.[6] The absence of any significant frequency dependence to the measured conductivity in pure samples provides strong evidence against disorder limited transport so that the value of $E_{sp} = 0.7$ eV may be considered the intrinsic value.

The values obtained from the reflectance for ω_p and ω_{sp} are consistent with the single-particle gap of 0.7 eV[6] determined from the conductivity, and with the microwave dielectric constant. Inserting the above values for ϵ_{core}, ω_p, and ω_{sp} into Eq. (2) gives $\epsilon_1 = 3.8$. However, if the dc conductivity value of 0.7 eV is used for the gap, Eq. (2) gives $\epsilon_1 = 5.4$, in excellent agreement with the measured value. The optical value for ω_p is somewhat uncertain as noted above, since it may more properly be considered as an average gap rather than the minimum direct gap. The high density of states at the band edges, however, implies that the error introduced is small compared to the bandwidth and is expected to be of order 0.1 eV in this case. The optical value for $\omega_g \sim U$ is expected, moreover, to be somewhat larger than the low frequency value because of polaron effects. The phononic polaron binding energy of neutral TCNQ has been shown[16] to be of order 0.1 eV. The Coulomb interaction, and hence the single-particle

FIG. 2. Reflectance spectra of $K^+(TCNQ)^-$: (a) polarization parallel to chain axis; (b) polarization perpendicular to chain axis. Dashed line represents least-squares fit of Eq. (1) to the parallel polarized spectrum.
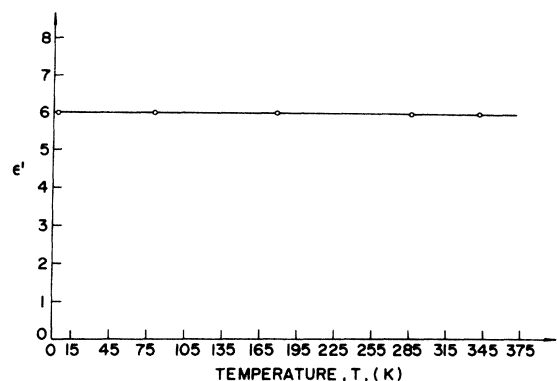
FIG. 3. Temperature dependence of the microwave dielectric constant of $K^+(TCNQ)^-$ over the range $4.2 < T < 350$ K.

gap, is expected to be reduced by twice this amount at frequencies much less than the vibrational frequencies of the molecule. Thus, the optically measured gap should be corrected for polaron effects before inferring the dielectric constant at low frequencies. The values for E_{sp} inferred from conductivity,[6] optical, and dielectric-constant measurements, then, are consistent within experimental errors of order 0.1 eV.

On the other hand, assuming the smaller value of $E_{sp} = 0.18$ eV as obtained by Vegter and Kommandeur,[3] one estimates $\epsilon_1 \sim 85$, i.e., more than an order of magnitude too large. Even more significant in this comparison is the observed temperature independence of ϵ_1. Using the single-particle analysis of Kommandeur et al.,[3] one finds a temperature-dependent energy gap and predicts an increase in ϵ_1 by a factor of 4 on going from 77 to 350 K, since the gap renormalizes as the tempera-

ture approaches the magnetic transition near 400 K. On the contrary, the experimental value for ϵ_1 is constant throughout the temperature interval, consistent with the existence of a relatively large single-particle gap which is essentially unaffected by the behavior of the magnetic excitations.

The spin-resonance spectrum of $K^+(TCNQ)^-$ at room temperature is shown in Fig. 4, and consists of a single narrow line ($g = 2$) with no evidence of sideband structure. Studies with high sensitivity show that any extra lines in the spectrum must be weaker than the main line by a factor exceeding 10^3. We conclude that the extra lines observed by Hibma[10] in $K^+(TCNQ)^-$ are not intrinsic, but result from impurities. The signal decreases exponentially in magnitude with decreasing temperature with an activation energy consistent with other measurements.[2,6]

However, a detailed understanding of the magnetic excitations is not available. The absence of dipolar splittings in the spin-resonance spectrum continues to be a puzzle, although triplet exciton delocalization toward the conventional spin-wave limit where dipolar splittings are not expected appears to be the most reasonable suggestion.

As noted above, the gap energy $\hbar\omega_g$ gives a rough measure of the effective Coulomb repulsion U_{eff}. The optical results, then, offer strong additional evidence of a large U_{eff} in $K^+(TCNQ)^-$. The plasma frequency may be used to estimate the tight-binding transfer integral,[13,17] $t = \frac{1}{4}W$, as about a tenth of an electron volt. Thus, $U_{eff} \sim W$ and the intermediate-to strong-coupling limit should apply. A similar conclusion was reached[7] regarding $Li^+(TCNQ)^-$ by analyzing the temperature dependence of the spin susceptibility.

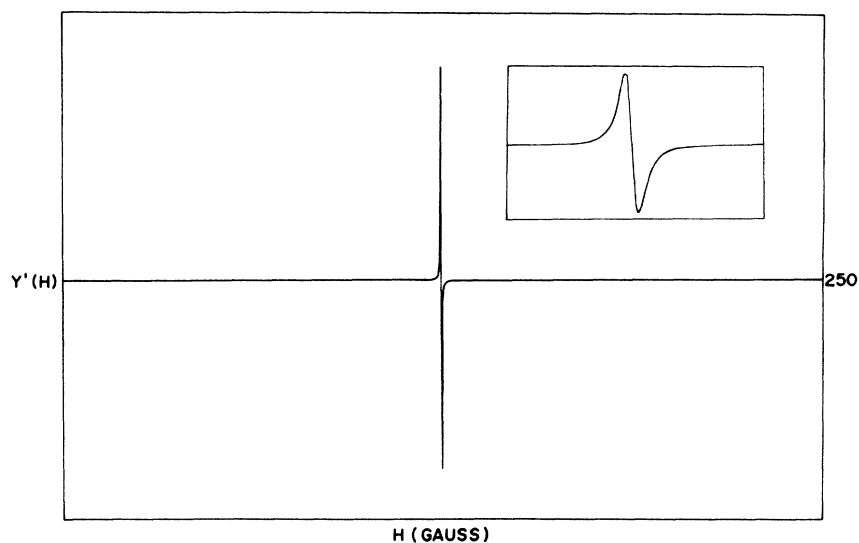Further support for this conclusion comes from

H (GAUSS)

FIG. 4. Spin-resonance spectrum of $K^+(TCNQ)^-$, showing single line with no evidence of sideband structure. Inset: expanded view of the resonance line (sweep range: 5 G).

the observation that $U_{eff} \lesssim \hbar\omega_p$. This has the consequence that plasmons are unable to screen the Coulomb repulsion effectively as described above. The electrons are localized with relatively long-range Coulomb correlations.

It is instructive to compare these data with the experimental situation in (TTF)(TCNQ). In this system, the Coulomb correlation effects are small.[18] A small energy gap is observed below 60 K, with equal single-particle and magnetic gap values.[9,19,20] The optical spectrum shows no evidence of an energy gap above 0.2 eV,[13] and a plasma edge is found at 0.8 eV.[13,17] The weak-coupling

limit, then, is appropriate in the case of (TTF) (TCNQ). The low value of U_{eff} is attributable to the metallic screening and the low-frequency reduction by exciton polarizability in the relatively tightly packed structure.[21]

The polarized reflectance spectrum and microwave dielectric constant measurements, then, confirm that the intermediate- to strong-coupling regime is appropriate to $K^+(TCNQ)^-$. The data show that $U_{eff} \sim W$ and $U_{eff} \lesssim \hbar\omega_p$, and confirm that $E_{sp} > E_m$. These results indicate that strong Coulomb correlations are important in this system and that a simple semiconductor model is inadequate.

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